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DE-A- 3 630 682
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Description

This invention relates to a process for the extrusion of polyethylene, which has a density equal to or less than about 0.915 gram per cubic centimetre (low density polyethylene).

The low modulus of commercial rubbers such as ethylene/propylene copolymers (EPM) and plasticized polyvinyl chloride (PVC) make these rubbers very useful in such applications as hose and tubing. In addition, PVC finds extensive use in film and other applications in which compliance with Food & Drug Administration (FDA) requirements is necessary. Because of its higher modulus, polyethylene including low density polyethylene has found limited utility in the aforementioned applications even though it has other advantageous qualities such as toughness and chemical resistance.

DE-A-3 630 682 discloses an extrusion process comprising blending low density polyethylene with an additive comprising corn oil, polybutene, stearate, petroleum resin and extruding the blend. The product may be used as an improved food wrapping film.

An object of this invention, therefore, is to provide a process which will not only serf to extrude the polyethylene into, for example, hose, tubing, and film but will reduce its modulus to a level at which it will be competitive with its EPM and PVC counterparts.

Other objects and advantages will become hereinafter.

According to the present invention, there is provided an extrusion process comprising blending a copolymer of ethylene and a minor amount of one or more alpha-olefins having at least 4 carbon atoms, said copolymer having a density equal to or less than 0.915 gram per cubic centimetre; a molecular weight in the range of 150,000 to 300,000; and a melt index in the range of from 0.05 to 1.5 gram per 10 minutes as determined under ASTM D-1238, Condition E, with a liquid hydrocarbon oil having a viscosity of at least 2500 SUS (Saybolt Universal Seconds) at 37.8 °C in an amount of 5 to 20 parts by weight of oil per 100 parts by weight of copolymer; and extruding the blend.

The copolymer of ethylene and an alpha olefin having less than 4 carbon atoms is termed low density polyethylene herein. The copolymer comprises a minor amount of one or more alpha-olefins having at least 4 carbon atoms, and preferably having 4 to 8 carbon atoms. The low density polyethylene can be prepared by the process described in EP-A-No.0 120 501 published on October 3, 1984.

The low density polyethylene can be in the form of porous granules or pellets. The porous granules of the low density polyethylene generally have a diameter in the range of about 25 micrometres to about 2500 micrometres. Regardless of its form, the low density polyethylene has a density equal to or less than about 0.915 gram per cubic centimetre, preferably in the range of 0.870 to 0.915 gram per cubic centimetre. If the low density polyethylene is in pallet form, the blending step is carried out with the polyethylene in the molten state.

The molecular weight of the low density polyethylene can be in the range of 150,000 to 300,000 and is preferably in the range of 150,000 to 250,000. Thus, the melt index is preferably in the range of 0.1 to 1.5 grams per 10 minutes. Melt index is determined under ASTM D-1238, Condition E. It is measured at 190°C and reported as grams per 10 minutes.

The portion of the copolymer attributed to the alpha-olefin comonomers can be in the range of 5 to 50 percent by weight based on the weight of the copolymer and is preferably in the range of 10 to 30 percent by weight based on the weight of the copolymer. The balance of the copolymer is based on ethylene. The preferred comonomers are 1-butene, 1-hexene, and 1-octene.

The liquid hydrocarbon oil is generally a petroleum derived processing oil commonly used in the compounding and extruding of rubber compositions. The major oil type present in any of these oils can be aromatic or aliphatic. Examples of these liquid hydrocarbon oils are paraffin oils, naphthenic oils, and mineral oils. Liquid polybutene can also be included among the examples. Mixtures of the various oils can be used, if desired. The oils can have preferably a viscosity upto 3000 SUS at 100 °F (37.8 °C).

In the case of porous granular low density polyethylene, the oils are usually dry blended with the polyethylene prior to extrusion (preblending), but the oil and resin can be blended in the extruder itself, if desired. Preblending is preferable, however, since it shortens the mixing time and is a key factor in achieving uniform distribution of the oil in the resin. In the case of pelletized low density polyethylene, the low density polyethylene is in the molten state when the blending is initiated. The amount of oil introduced into the blend of is in the range of 5 to 20 parts by weight of oil per 100 parts by weight of low density polyethylene. The low density polyethylene mixes readily with the oil without the use of heat except, as noted, when it is in pelletized form. Mixers and extruders useful in carrying out the process of the invention are conventional off-the-shelf equipment. A typical extruder is described in US patent 4,857,600. Mixers, which can be used to blend the resin and the oil, are Banbury or other internal mixers, two roll mills, or Baker Perkins or similar sigma blade mixers. As noted, extruders can also be used to mix the resin and the

oil.

Advantages of the blend are improved processability in the extruder, e.g., a fractional melt index will display the extrusion behavior of a 1 to 2 melt index resin; avoidance of bleeding when oil is used in preferred amounts; extrusion can be conducted under less pressure and amperage without sacrificing production rates; hose and tubing made from the combination of high molecular weight low density polyethylene and oil, when compared to plasticized PVC, have a lower brittle point, a higher softening temperature, and better chemical and environmental resistance; and, with respect to extruded film, the oil modified low density polyethylene displays improved puncture dart drop and clarity. The production of film from the oil modified low density polyethylene is particularly useful in the preparation of products, which must meet FDA requirements. Thus, a low density polyethylene with, for example, a 0.910 g/cc density, which meets FDA requirements, can be blended with an oil, which also meets FDA requirements. The result is a product which has the properties of a low density polyethylene having a lower density than 0.910 g/cc and still meets the FDA requirements.

Polyethylenes, in general, display poor compression set and resiliency. Compression set, which is determined under ASTM-D-395-85, is defined as the amount (in percent) by which a standard test piece fails to return to its original thickness after being subjected to a standard compression load for a fixed period of time. The better the compression set, i.e., the lower the percent, the more resilient the polymer. One more advantage of the oil modified low density polyethylene is its improved compression set relative to the unmodified low density polyethylene. The compression set is further improved by crosslinking the oil modified low density polyethylene.

Crosslinking is accomplished by using conventional techniques. The oil modified low density polyethylene can be crosslinked by adding a crosslinking agent to the composition or by making the resin hydrolyzable, which is accomplished by adding hydrolyzable groups, such as $-Si(OR)_3$ wherein R is a hydrocarbyl radical, to the resin structure through copolymerization or grafting.

Suitable cross linking agents are organic peroxides such as dicumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; t-butyl cumyl peroxide; and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3. Dicumyl peroxide is preferred.

Hydrolyzable groups can be added, for example, by copolymerizing ethylene with an ethylenically unsaturated compound having one or more $-Si(OR)_3$ groups such as vinyltrimethoxysilane, vinyltriethoxysilane, and gammamethacryloxypropyl-trimethoxysilane or by grafting these silane compounds to the resin in the presence of the aforementioned organic peroxides. The hydrolyzable resins are then crosslinked by moisture in the presence of a silanol condensation catalyst such as dibutyltin dilaurate, dibutyltin diacetate, stannous acetate, lead naphthenane, and zinc caprylate. Dibutyltin dilaurate is preferred.

Conventional additives can be added to the oil modified low density polyethylene during the preblending step and/or the extrusion step. The amount of additive is usually in the range of 0.01 to 60 percent by weight based on the weight of the resin. Useful additives are antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents, vulcanizing agents, crosslinking agents, crosslinking catalysts, and crosslinking boosters.

The invention is illustrated by the following examples.

Examples 1 to 4

Porous granular low density polyethylene having a density of 0.910 gram per cubic centimeter and prepared using the catalyst and process described in European Patent Application 0 120 501, referred to above, is used in the examples. The comonomer is 1-hexene. The oil is a paraffin oil having a viscosity of 2540 SUS at 37.8 °C (100 °F).

The low density polyethylene and the oil are mixed in a ribbon blender for 15 minutes. The mixture is then pelletized, and the pellets are extruded in an extruder to provide a film having a thickness of 0.025mm (0.001 inch). The extruder operates at 60 revolutions per minute, the die gap (or die diameter) in the extruder is 0.025mm (0.001 inch); and the BUR is 2:1. The BUR is the blow-up ratio. This is the ratio of die diameter to bubble diameter. The bubble diameter is 2 X layflat/pi. The "layflat" refers to the width of the flattened bubble.

It is found that the modulus of the oil modified low density polyethylene is approximately the same as otherwise equivalent commercial EPM's and PVC's.

Variables and conditions are set forth in the Table:

TABLE

Example	1*	2	3*	4
Melt index (g/10 min)	1	1	0.5	0.5
amount of oil (1% by wt)	0	10	0	10
pressure kPa (psig)	16649 (2400)	13201 (1900)	17339 (2500)	13891 (2000)
melt temperature $^oC(^oF)$	229 (444)	224 (435)	230 (246)	225 (437)
amps	13.5	11.6	13.8	12.2
production rate kg/hr (lbs/hr)	12.09 (26.6)	12.8 (28.2)	12.05 (26.5)	12.55 (27.6)

NOTES TO TABLE:

1. Melt index is determined as noted above.
2. The amount of oil is the percent by weight oil based on the combined weight of the low density polyethylene in the oil.
3. Amps refers to the current passing through the drive motor, which turns the screw.
4. The production rate is the number of kg (pounds) of film produced by the extruder per hour.

* comparison

Claims

1. An extrusion process comprising:
   (i) blending a copolymer of ethylene and a minor amount of one or more alpha-olefins having at least 4 carbon atoms, said copolymer having a density equal to or less than 0.915 gram per cubic centimetre; a molecular weight in the range of 150,000 to 300,000; and a melt index in the range of from 0.05 to 1.5 grams per 10 minutes as determined under ASTM D-1238, Condition E, with a liquid hydrocarbon oil having a viscosity of at least 2500 SUS (Saybolt Universal Seconds) at 37.8 °C in an amount of 5 to 20 parts by weight of oil per 100 parts by weight of copolymer; and
   (ii) extruding the blend.

2. A process as claimed in claim 1 wherein the copolymer is in a porous granular form.

3. A process as claimed in claim 1 or claim 2 wherein the blending is conducted with the copolymer in the molten state.

4. A process as claimed in any one of the preceding claims wherein the density of the copolymer is above about 0.870 gram per cubic centimetre.

5. A process as claimed in any one of the preceding claims wherein the molecular weight is in the range of from 150,000 to 250,000.

6. A process as claimed in any one of the preceding claims wherein the melt index of the copolymer is in the range of from 0.1 to 1.5 grams per 10 minutes.

7. A process as claimed in any one of the preceding claims wherein the oil is a paraffin oil, a naphthenic oil, a mineral oil, polybutene, or a mixture of two or more of such oils.

8. A process as claimed in any one of the preceding claims wherein the copolymer and the oil are blended in an extruder.

9. A process as claimed in any one of the preceding claims wherein a cross linking agent is blended with the copolymer or incorporated into the mixture of copolymer and oil during extrusion, and cross linking of the copolymer is effected either during or after extrusion.

10. Process as claimed in any one of the preceding claims for producing an extruded product in the form of a hose, tubing or film.

Patentansprüche

1. Extrusionsverfahren, umfassend
   (i) Vermischen eines Copolymers aus Ethylen und einer kleineren Menge eines oder mehrerer α-Olefine mit mindestens 4 Kohlenstoffatomen, wobei das Copolymer eine Dichte gleich oder kleiner als 0,915 g/cm³, ein Molekulargewicht im Bereich von 150 000 bis 300 000 und einen Schmelzindex im Bereich von 0,05 bis 1,5 g pro 10 Minuten, bestimmt nach ASTM D-1238, Bedingung E besitzt, mit einem flüssigen Kohlenwasserstofföl mit einer Viskosität von mindestens 2500 SUS (Saybolt Universal Seconds) bei 37,8 °C in einer Menge von 5 bis 20 Gew.-Teilen Öl pro 100 Gew.-Teile Copolymer und
   (ii) Extrudieren des Gemisches.

2. Verfahren nach Anspruch 1, wobei das Copolymer in Form eines porösen Granulats vorliegt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei das Vermischen mit dem Copolymer in geschmolzenem Zustand durchgeführt wird.

4. Verfahren nach einem der vorangehenden Ansprüche, wobei die Dichte des Copolymers oberhalb etwa 0,870 g/cm³ liegt.

5. Verfahren nach einem der vorangehenden Ansprüche, wobei das Molekulargewicht im Bereich von 150 000 bis 250 000 liegt.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei der Schmelzindex des Copolymers im Bereich von 0,1 bis 1,5 g je 10 Minuten liegt.

7. Verfahren nach einem der vorangehenden Ansprüche, wobei das Öl ein Paraffinöl, ein naphthenisches Öl, ein Mineralöl, Polybuten oder ein Gemisch aus zwei oder mehreren derartigen Ölen ist.

8. Verfahren nach einem der vorangehenden Ansprüche, wobei das Copolymer und das Öl in einem Extruder vermischt werden.

9. Verfahren nach einem der vorangehenden Ansprüche, wobei ein Vernetzungsmittel mit dem Copolymer vermischt oder in das Gemisch aus Copolymer und Öl während der Extrusion eingebaut wird und das Copolymer entweder während oder nach dem Extrudieren vernetzt wird.

10. Verfahren nach einem der vorangehenden Ansprüche zur Herstellung eines extrudierten Produktes in Form eines Schlauchs, Rohrs oder einer Folie.

Revendications

1. Procédé d'extrusion, comprenant les étapes consistant :
   (i) à mélanger un copolymère d'éthylène et d'une petite quantité d'une ou plusieurs alpha-oléfines ayant au moins 4 atomes de carbone, ledit copolymère ayant une masse volumique égale ou inférieure à 0,915 g/cm^3 ; un poids moléculaire compris dans l'intervalle de 150 000 à 300 000 ; et un indice de fluidité compris dans l'intervalle de 0,05 à 1,5 g pour 10 minutes, déterminé suivant la condition E de la norme ASTM D-1238, avec une huile hydrocarbonée liquide ayant une viscosité d'au moins 2500 SUS (Secondes Universelles Saybolt) à 37,8 °C en une quantité de 5 à 20 parties en poids d'huile pour 100 parties en poids de copolymère ; et
   (ii) à extruder le mélange.

2. Procédé suivant la revendication 1, dans lequel le copolymère est sous forme granulaire poreuse.

3. Procédé suivant la revendication 1 ou la revendication 2, dans lequel le mélange est effectué avec le copolymère à l'état fondu.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la masse volumique du copolymère est supérieure à environ 0,870 g/cm^3.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le poids moléculaire est compris dans l'intervalle de 150 000 à 250 000.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'indice de fluidité du copolymère est compris dans l'intervalle de 0,1 à 1,5 g pour dix minutes.

7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel l'huile est une huile paraffinique, une huile naphténique, une huile minérale, un polybutène ou un mélange de 2 ou plus de 2 de ces huiles.

8. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le copolymère et l'huile sont mélangés dans une extrudeuse.

9. Procédé suivant l'une quelconque des revendications précédentes, dans lequel un agent de réticulation est mélangé au copolymère ou incorporé au mélange de copolymère et d'huile au cours de l'extrusion, et la réticulation du copolymère est effectuée pendant ou après l'extrusion.

10. Procédé suivant l'une quelconque des revendications précédentes, pour la formation d'un produit extrudé sous forme d'un tuyau souple, d'un tube ou d'un film.